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In-situ growth of platinum with hierarchical porosity for low impedance biomedical microelectrode fabrication.

Frederik Ceyssens[a,*], Sreeprasanth Pulinthanathu Sree[b], Lisa Geerts[b] , Johan Martens[b], Robert Puers[a]

[a]*KULeuven, dept ESAT-MICAS, Leuven, Belgium*
[b]*KULeuven, Centre for Surface Chemistry and Catalysis, Leuven, Belgium*

Abstract

We report a novel process that allows depositing hierarchically porous platinum, i.e. platinum with structured pores from about 1 micron down to 3 nm in porosity, in situ on flexible microelectrodes. The process is based on molecular self-assembly of a porous silica zeotile, which is then deposited on the electrode contacts of flexible platinum electrode arrays fabricated with classic lithographic techniques. The pores are then Pt filled using atomic layer deposition (ALD) and the silica mold is removed chemically. Compared to our earlier work, the in-situ ALD step improves adhesion and allows a lower temperature budget as no sintering is required. An up to 1000x reduction in electrode impedance was measured as well as a 12x increase in charge injection capacity.

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Keywords: Hierarchically porous; electrodes; nanoporous; electrical stimulation;

1. Introduction

In biomedical microdevices such as neural implants, retinal implants and labs-on-a-chip, electrical stimulation and recording are gaining more and more importance. The use of planar metal electrodes often constraints further miniaturization, as impedances go up and charge injection capability goes down approximately linearly with area. A range of techniques to improve impedance has been presented, typically aiming at increasing the accessible surface area and/or introducing materials on whose surfaces reversible reactions can occur. Notable examples include porous Pt [1], TiN[2], iridium oxide[2], carbon nanotubes [3] and polymers such as PEDOT [4].

In our research, we explore the use of hierarchically porous materials on electrode surfaces in order to improve

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the accessibility of the material by the surrounding liquid. This means that the electrode will have relatively large channels, which branch into smaller channels that branch again into smaller channels. Having this combination of microscale and nanoscale features would allow the liquid to penetrate deeply into the electrode layer, while still increasing the available surface orders of magnitude. In non-hierarchically porous electrodes such as IrOx, the effect of increasing the layer thickness tends to flatten out from a thickness of about 500 nm on [5].

In our previous work, we achieved hierarchically porous platinum structures by attaching a platinum nanopowder on planar electrodes [6] by sintering. However, the adhesion was not sufficient for implant use even at relatively high sintering temperatures.

In this follow-up work, we explore the use of in-situ atomic layer deposition (ALD) of a platinum layer in a hierarchically porous molded structure, deposited on the wafer in a foregoing step on plain platinum electrode structures. This way, the porous Pt layer gets seamlessly connected to the plain platinum underneath which was hypothesized to improve adhesion. Furthermore, no high temperature steps would be required as the highest temperature step, the ALD process, is executed at 300°C.

2. Experiments

2.1. Electrode fabrication

A 7.5 micron thick, polyimide-insulated, planar flexible electrode array with 350 µm diameter Pt electrodes was fabricated by classic lithographic techniques on a 4 inch silicon wafer (figure 1, a-e). The process is detailed in [7]. Then, a hierarchically porous silica mold (zeotile), fabricated by molecular self-assembly, is deposited (figure 1, f). The zeotile is fabricated as in [6] and a SEM image is shown in figure 2. The zeotile was deposited on the electrodes by micropipetting while being suspended in a 3 wt% concentration in water. A volume of 0.1 µL per 350 µm diameter electrode was used, while the substrate was heated to 90°C to accelerate drying.

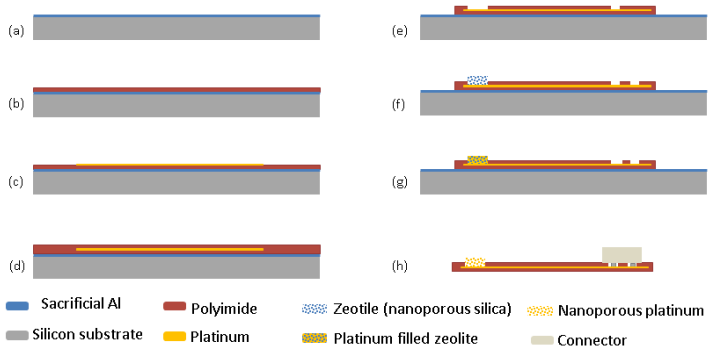

Fig. 1. Flexible electrode fabrication. (a) Si wafer with sacrificial Al layer (b) deposition of lower PI layer (c) deposition and patterning of Pt layer by lift-off processing and sputtering (d) deposition of upper PI layer (e) RIE etch to pattern PI layer and release Pt (f) deposition of zeotile suspension (g) ALD based filling of zeotile mold (f) mold release and release from wafer.

Afterwards, platinum is deposited in situ by ALD, whereby the deposited layer directly gets linked to the supporting planar electrode (figure 1, g). A Sentech SI ALD system was used. A thermal ALD [8][9] process was selected as plasma processes tend to have an inferior isotropy. The process used is based on methylcyclopentadienyltrimethylplatinum ($MeCpPtMe_3$) and oxygen and is summarized in table 1 and deposits about 7 nm of Pt. The main concerns in the process designs were the need for a relatively high O_2 pressure (> 80 Pa) to allow the Pt precursor decomposition to fully proceed, and increased waiting and incubation times to allow the penetration of the precursor deeply into the pores of the zeotile.

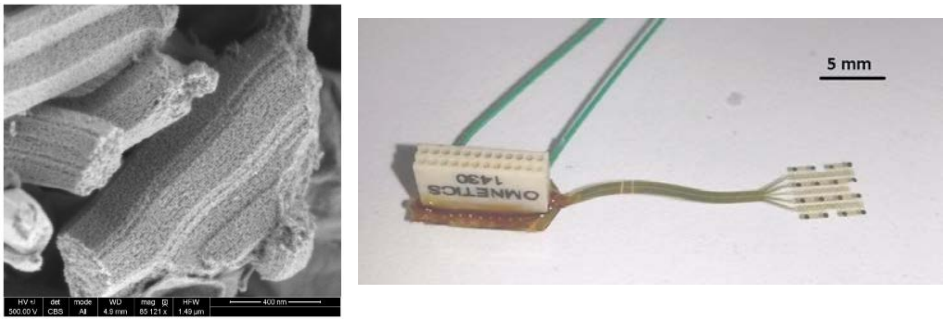

Fig. 2. Left: SEM image of produced zeotile silica powder, showing the hierarchical porosity.
Right: Flexible electrode array after fabrication process

After the ALD step, sputter etching (100" 100W sputter etch bij 50 sccm Ar, in JLS sputter etcher) was used to remove the platinum on plain surfaces. This also opens up the top of the zeotile mold, exposing silica for subsequent wet etching. Finally, a HF etch (140 minutes in 7:1 BHF followed by a 10' rinse in DI water) removes the silica mold and the arrays can be released from the carrier wafer. The result of the fabrication procedure is shown on the right part of figure 2.

Table 1. ALD deposition process. Steps 2-3 are repeated 100x. Wafer temperature is 300°C, sidewalls are at 150 °C.

Step	Parameters
Conditioning	5' in 200W O2 plasma, 200 sccm.
Pt precursor	Close throttle valve. Open N2 flow, 40 sccm. After 2", open Pt precursor valve for 50 ms. After 6", stop N2 flow. Wait 30". Repeat 3x.
O2 step	Put throttle valve at 5%. 30" of O2 flow at 70 sccm. Wait 25" with throttle at 100%.

2.2 Characterization

After the fabrication as described above, impedance spectroscopy and cyclic voltammetry in phosphate buffered saline (pH 7.2) were performed. A Princeton Applied Research Versastad 200 potentiostat was used, with a 2 cm^2 Pt counter electrode and a Ag/AgCl reference electrode.

The results are shown on figure 3. The coating was shown to decrease impedance with three orders of magnitude below 100 Hz compared to plain Pt electrodes of the same area. Cyclic voltammetry performed at 10 mV/sec shows a 12x increased charge capacity. The adhesion of the layer was also tested. The previous, sintering-based process yielded layers with very low adhesion: the layers could be removed from the surface by a low-pressure water jet or by mild scratching. This made the adhesion difficult to quantify. The adhesion of the new layers was such that they could be tested by putting them through harsher mechanical tests. A treatment in an ultrasonic bath for one minute was selected for this. Though the layers were still present after this test, there was still an increase in impedance noticeable: after ultrasonic treatment the layers only showed a two orders of magnitude impedance improvement at low frequencies instead of three orders of magnitude as before, compared to planar Pt electrodes.

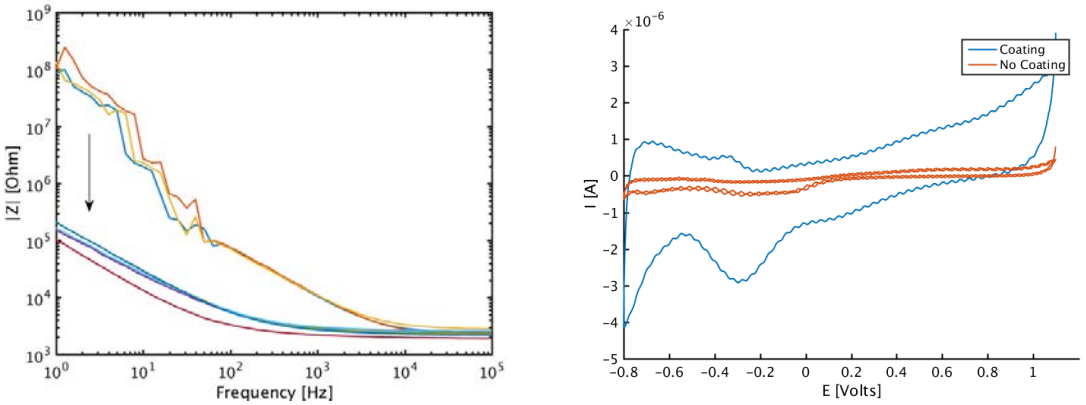

Fig. 3. Left: measured impedance spectrum of uncoated (top lines) and coated (lower lines) microelectrodes. The porous Pt coating is seen to reduce impedance with up to 3 orders of magnitude. Right: measured cyclic voltammograms.

3. Discussion and conclusion

A novel method of fabrication of hierarchically porous electrodes was demonstrated and shows the ability to reduce electrode impedances with three orders of magnitude at low frequencies, compared to planar electrodes of the same material. The method was applied to the fabrication of flexible neural electrode arrays. Compared to our previous work, the adhesion and wafer-level fabrication compatibility have been improved. Though harsh treatment (sonification) still damages the layers, it the adhesion should now be sufficient in most practical applications. As the process stands now, the only serial step left is the micropipetting of the zeotile suspension. There are ways to perform this step to a parallel scale as well, for example by screenprinting the zeotile, suspended in a paste that decomposes at low temperature. For this, a carrier material such as polyethylene carbonate (PEC) is suitable [10]. The process demonstrated is not limited to Pt deposition as about 20 metals and a large set of compounds can be deposited by ALD [11]. As no lithography is required and ALD is a technique that can be applied to a wide range of surfaces, the potential application range of this fabrication method could be extensive. Next to the application in biomedical electrodes, they could be applied in batteries, fuel cells, (bio)chemical sensors and gas sensors.

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